Vapor-Induced Switching

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Water-Vapor-Induced Reversible Switching of Electronic States in an MMX-Type Chain Complex with Retention of Single Crystallinity**

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Response to external stimuli in the solid state is a significant phenomenon from the viewpoints of both fundamental and applied sciences. Especially the response to chemical stimuli, such as exposure to molecular vapor, has recently attracted much attention. Adsorption and desorption behaviors of porous coordination polymers (PCPs), or metal–organic frameworks (MOFs), have been the subject of intense study because they can be applied not only in chemical applications, such as storage,[1] separation,[2] and catalysis,[3] but also in switching of the physical properties, such as magnetism,[4] photoluminescence,[5] and electrical conductivity.[6] To switch the physical properties, the materials must be responsive to structural perturbations. From this point of view, a one-dimensional (1D) electron system is attractive because its electronic states strongly correlate with the lattice freedom.[7] In addition, since many 1D compounds have interesting optical,[8] conductive,[9] and magnetic[10] properties, they have great potential to be used as multifunctional switching materials responsive to guest molecules.

To date, several compounds with 1D electron systems have been reported to undergo guest dehydration–rehydration.[11] However, these materials are no longer single crystals after the dehydration, which makes it difficult to investigate precisely the changes in the structure and electronic states. For the first time, to our knowledge, reversible water-vapor-induced switching of the electronic state and physical properties of a quasi-1D halogen-bridged dinuclear metal complex (MMX chain) that retains its single crystallinity is reported.

On the basis of theoretical calculations and experimental data, the electronic states of the MMX chains can be classified into the following four states and are known to be strongly correlated to the position of the bridging halide ion.[12]

a) Average-valence (AV) state
$-M^{2.5+}-M^{2.5+}-X-M^{2.5+}-M^{2.5+}-X-$
b) Charge-density-wave (CDW) state
$\cdots M^{2+}-M^{2+}\cdots X-M^{3+}-M^{3+}-X\cdots$
c) Charge-polarization (CP) state
$\cdots M^{2+}-M^{3+}-X\cdots M^{2+}-M^{3+}-X\cdots$
d) Alternating charge-polarization (ACP) state
$\cdots M^{2+}-M^{3+}-X-M^{3+}-M^{2+}\cdots X\cdots$

MMX chains synthesized to date have been categorized by the two ligand systems used: dithioacetate (dta) $[M_2(RCS_2)_4I]$ (M = Ni, Pt; R = alkyl)[13] and diphosphite (pop) $A_4[Pt_2(pop)_4X]\cdot n\,H_2O$ (A = alkali metal, alkyl ammonium, etc.; X = Cl, Br, I; pop = $P_2H_2O_5^{2-}$).[14] We studied the pop system because its electronic state can be controlled by introducing various countercations and removing lattice water.

Herein, we study the water-vapor-induced switching of the electronic states and physical properties of $K_2(H_3NCH_2CHXCH_2NH_3)[Pt_2(pop)_4I]\cdot 4\,H_2O$ (X = Me (**1**·4 H_2O), H (**2**·4 H_2O), Cl (**3**·4 H_2O)). As reported,[15] **1**·4 H_2O is in a new ACP + CDW electronic state. Since the crystal structure of **3**·4 H_2O was isomorphic to **1**·4 H_2O, it was concluded that the electronic state of **3**·4 H_2O was also an ACP + CDW state (see the Supporting Information). The crystal structure of **2**·4 H_2O (Figure 1 a,c) was similar to that of **1**·4 H_2O and **3**·4 H_2O except that the crystal system was orthorhombic and that the position of the bridging I^- ion was disordered.[17] Two different Pt-I-Pt distances (*d*(Pt-I-Pt)) caused a two-fold periodicity along the chain axis, which is characteristic of an ACP state. However, two signals (ν(Pt–Pt)) were observed in the polarized Raman spectrum (Figure S3 in the Supporting Information), thus indicating that there are two inequivalent $\{Pt_2(pop)_4\}$ units, which is characteristic of a CDW state.[16] Therefore, **2**·4 H_2O was also concluded to be in an ACP + CDW state.

To eliminate the water molecules from complexes **1**–**3**·4 H_2O, single crystals were heated at 70 °C under vacuum (less than 100 Pa) for a day. Dried crystals of **1** and **3** were polycrystalline, whereas that of **2** was still single-crystalline. In other words, it was suitable for X-ray single-crystal structure analysis. Figure 1 a,b shows crystal structures of **2**·4 H_2O and **2**. All water molecules in the 1D cavity surrounded by coordination bond networks among the $\{Pt_2(pop)_4\}$ units and K^+ ions were removed by heating under vacuum. As shown in Figure 1 c,d, **2** lost the two-fold periodicity along the *c* axis,

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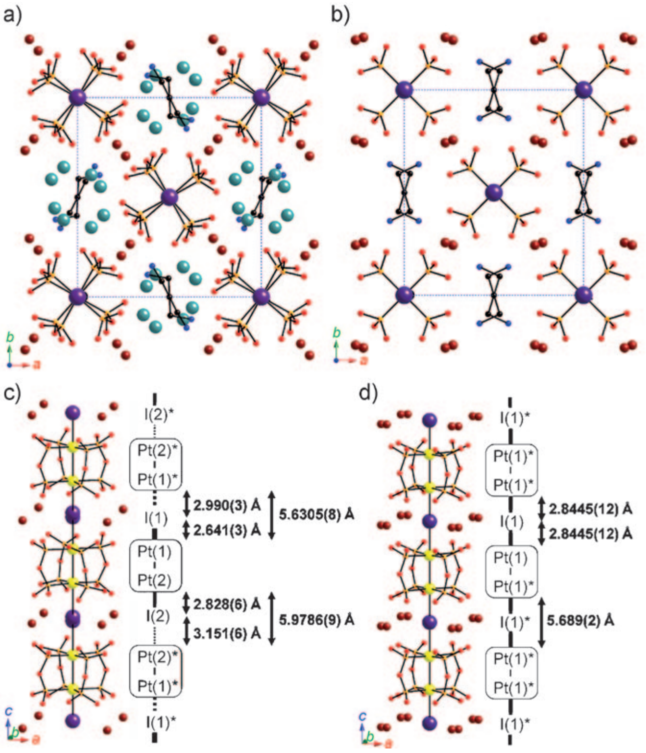

Figure 1. Crystal structures of a, c) **2**·4 H_2O and b, d) **2**. The chain structure, Pt–I, and Pt-I-Pt distances are described in (c) and (d). H atoms in (a–d) and H_2O molecules and $H_3NC_3H_6NH_3^{2+}$ ions in (c) and (d) are omitted for clarity. I(1) and I(2) of **2**·4 H_2O and K^+ ions of **2** are disordered. Pt yellow, I purple, K brown, P orange, O (ligand) red, O (H_2O) light blue, N blue, C black.

and there is only one d(Pt-I-Pt). In other words, **2** is no longer in an ACP + CDW state. The electronic state of **2** will be discussed below. The estimated crystal structures of **1** and **3** and the role of coordination-bonding networks around the K^+ ion on the dehydration process are discussed in the Supporting Information.

Next, we exposed **1**–**3** to H_2O vapor for a day. From the XRD patterns (Figures S4, S6, S7 in the Supporting Information), the crystal structures of the rehydrated complexes were identical to those of the initial complexes, thus indicating that dehydration–rehydration in **1**–**3**·4 H_2O is reversible. To our knowledge, **2**·4 H_2O is the first complex with a 1D electron system to maintain single crystallinity during dehydration and rehydration.

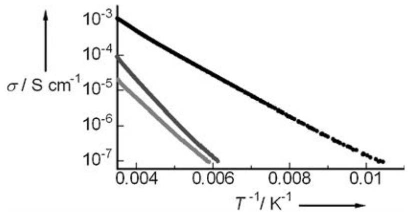

Figure 2. Temperature dependence of the electrical conductivity of initial (dark gray) and rehydrated (light gray) complex **2**·4 H_2O and dehydrated (black) complex **2**.

To determine the differences in physical properties, we measured the temperature dependence of the electrical conductivity parallel to the chain c axis of **1**–**3**·4 H_2O (initial and rehydrated states) and **1**–**3** (dehydrated state) by using a two-probe method. The results for **2**·4 H_2O and **2** are shown in Figure 2; the electrical conductivity at room temperature increased by approximately 50 times, and the activation energy (E_a) decreased by half after dehydration. These values nearly returned to the initial ones after rehydration. The higher conductivity of **2** can be explained by an increase in the orbital overlap between the Pt ($5d_{z^2}$) and I ($5p_z$) atoms owing to a shorter d(Pt-I-Pt). Similar results were obtained for **1**·4 H_2O, **3**·4 H_2O, **1**, and **3** (Figure S10 in the Supporting Information).

Since the crystal structure of **2** could be fully determined, we focused on complex **2**·4 H_2O and **2** to investigate the changes in the electronic states. d(Pt-I-Pt) of **2** (5.689(2) Å) is the shortest of all of the MMX chains reported to date, and the I^- ion is located at the midpoint between neighboring {$Pt_2(pop)_4$} units without disorder. These structural features of **2** are characteristic of the AV state. However, there is still a possibility that the disorder of the bridging I^- ion was beyond the resolution of the X-ray single crystal analysis.

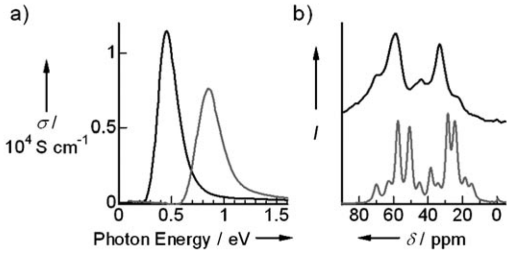

Figure 3. a) Optical conductivity spectra of **2**·4 H_2O (gray) and **2** (black) with the polarization of light parallel to the c axis at room temperature. b) ^{31}P MAS NMR spectra of **2**·4 H_2O (gray) and **2** (black) measured at room temperature in the solid state.

To confirm the electronic state of **2**, we acquired optical conductivity (Figure 3 a) and ^{31}P MAS NMR spectra (Figure 3 b) of both initial and dehydrated crystals. As shown in Figure 3 a, a red shift in the optical conductivity spectrum was observed upon dehydration. The charge-transfer energy (E_{CT}) determined from the peak decreased from 0.85 to 0.45 eV. This decrease indicates a decrease in band gap owing to two effects: 1) an increase in the bandwidth caused by an increase in the transfer integral along the chain axis and 2) a decrease in the energy difference between the HOMO and LUMO comprised of Pt(d_σ*) orbitals caused by a decrease in the electron–phonon interaction.[12,13b] The E_{CT} of **2** was the smallest of all MMX chains in the pop system, although it is larger than that of [$Pt_2(dta)_4I$] (0.3 eV), which is in an AV state.[13b]

Figure 3 b shows ^{31}P MAS NMR spectra of **2**·4 H_2O and **2**. As reported by Kimura et al.,[16] the ^{31}P chemical shift (δ) depends on the crystal field around the P atom and the charges of the Pt ions, and δ is larger for P atoms coordinated to Pt ions in lower oxidation states. Four intense peaks were observed in the ^{31}P MAS NMR spectrum of $\mathbf{2}\cdot 4\,H_2O$, indicating the existence of four inequivalent P atoms, which is consistent with the crystal structure. Satellite peaks arising from coupling between ^{31}P and ^{195}Pt were also observed. After dehydration, only two intense peaks were observed in the spectrum of **2**, indicating the existence of two sets of inequivalent P atoms. The large difference of δ between the peaks (26 ppm) is derived from Pt ions in different oxidation states. Moreover, in the polarized Raman spectrum of **2** (Figure S3 in the Supporting Information), two peaks were observed, indicating the existence of two different $\{Pt_2(pop)_4\}$ units. Therefore, we concluded that the electronic state of **2** was a CDW state. As shown in Figure S11 in the Supporting Information, the relationship between E_{CT} and d(Pt-I-Pt) of **2** was characteristic of a CDW state. Interestingly, the broadened peaks in the ^{31}P MAS NMR spectrum suggest the generation of paramagnetic spins. Since the CDW state is thought to be diamagnetic, paramagnetic spins should not be present.

To confirm the existence of paramagnetic spins, we measured the temperature dependence of the molar spin susceptibility (χ) of $\mathbf{2}\cdot 4\,H_2O$ and **2** using ESR spectroscopy (Figure 4). χ of $\mathbf{2}\cdot 4\,H_2O$ followed the Curie–Weiss law (solid line), amounting to 0.11 % magnetic impurities per $\{Pt_2(pop)_4\}$ unit. These impurities were ascribed to isolated Pt^{3+} ions created at the chain edges or at defect sites. Therefore, $\mathbf{2}\cdot 4\,H_2O$ is in a diamagnetic ACP + CDW state. On the other hand, χ of **2** gradually increased when $T > 70$ K, and χ followed the Curie–Weiss law (solid line in Figure 4) when $T < 70$ K, amounting to 0.018 % magnetic impurities per $\{Pt_2(pop)_4\}$ unit. To characterize this enhancement, we subtracted the Curie component (χ_c) from the observed χ and found that the resultant susceptibility ($\Delta\chi = \chi - \chi_c$) obeyed an activation-type equation above 70 K: $\Delta\chi T = C\exp(-E_g/k_B T)$, where C is the Curie constant of activated spins, E_g is the activation energy, and k_B is the Boltzmann constant. Therefore, it is thought that some thermally activated paramagnetic excited states caused by a decrease in the band gap energy contribute to the increase in χ. To clarify the origin of the paramagnetic spins and their electronic state in the excited states, more detailed ESR studies are currently in progress.

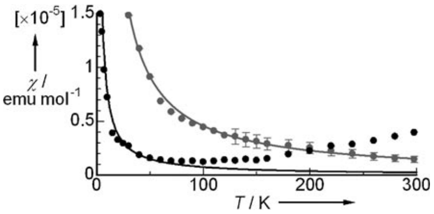

Figure 4. Temperature dependence of the molar spin susceptibility (χ) of $\mathbf{2}\cdot 4\,H_2O$ (gray) and **2** (black). The solid lines were fitted using the Curie–Weiss law. Only the data below 70 K were used for fitting of **2**.

In summary, a reversible structural change accompanied by changes in the electrical conductivity and optical gap was realized with the dehydration and rehydration of H_2O molecules from $K_2(H_3NCH_2CHXCH_2NH_3)[Pt_2(pop)_4I]\cdot 4\,H_2O$ (X = Me ($\mathbf{1}\cdot 4\,H_2O$), H ($\mathbf{2}\cdot 4\,H_2O$), Cl ($\mathbf{3}\cdot 4\,H_2O$)). A reversible change in the structure of $\mathbf{2}\cdot 4\,H_2O$ occurred without loss of single-crystallinity. Upon dehydration, the electronic state changed from an ACP + CDW state ($\mathbf{2}\cdot 4\,H_2O$) to a narrow-gapped CDW state (**2**). This water-vapor-induced switching opens a new avenue of research toward the design of multifunctional vapor-induced switching materials based on a strong correlation between the electrons and the lattice of 1D electron systems.

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[1] L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294–1314.
[2] J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
[3] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
[4] a) M. Kurmoo, *Chem. Soc. Rev.* **2009**, *38*, 1353–1379; b) M. Ohba, et al., *Angew. Chem.* **2009**, *121*, 4861–4865; *Angew. Chem. Int. Ed.* **2009**, *48*, 4767–4771. See the Supporting Information for the complete author list.
[5] a) M. Kato, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 287–294; b) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.
[6] a) Y. Fuma, M. Ebihara, S. Kutsumizu, T. Kawamura, *J. Am. Chem. Soc.* **2004**, *126*, 12238–12239; b) S. Takaishi, et al., *Inorg. Chem.* **2009**, *48*, 9048–9050.
[7] a) *Low-dimensional cooperative phenomena* (Ed.: H. J. Keller), Plenum, New York, **1975**; b) S. Kagoshima, H. Nagasawa, T. Sambongi, *One-dimensional conductors*, Springer, Berlin, **1988**.
[8] a) H. Kishida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi, Y. Tokura, *Nature* **2000**, *405*, 929–932; b) S. Iwai, H. Okamoto, *J. Phys. Soc. Jpn.* **2006**, *75*, 011007; c) S. Tao, T. Miyagoe, A. Maeda, H. Matsuzaki, H. Ohtsu, M. Hasegawa, S. Takaishi, M. Yamashita, H. Okamoto, *Adv. Mater.* **2007**, *19*, 2707–2710.
[9] a) J. P. Ferraris, D. O. Cowan, V. V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948–949; b) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Commun.* **1977**, 578–580.
[10] a) F. D. M. Haldane, *Phys. Rev. Lett.* **1983**, *50*, 1153–1156; b) R. Clerac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12837–12844.
[11] a) M. Yamashita, et al., *Angew. Chem.* **2004**, *116*, 4867–4871; *Angew. Chem. Int. Ed.* **2004**, *43*, 4763–4767; b) H. Mastuzaki, H. Kishida, H. Okamoto, K. Takizawa, S. Matsunaga, S. Takaishi, H. Miyasaka, K. Sugiura, M. Yamashita, *Angew. Chem.* **2005**, *117*, 3304–3307; *Angew. Chem. Int. Ed.* **2005**, *44*, 3240–3243; c) M. Yamashita, et al., *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1404–1406.
[12] a) M. Kuwabara, K. Yonemitsu, *J. Phys. Chem. Solids* **2001**, *62*, 435–438; b) M. Kuwabara, K. Yonemitsu, *J. Mater. Chem.* **2001**, *11*, 2163–2175.
[13] a) C. Bellitto, A. Flamini, L. Gastaldi, L. Scaramuzza, *Inorg. Chem.* **1983**, *22*, 444–449; b) H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukawa, T. Mitani, M. Seto, Y. Maeda, *J. Am. Chem. Soc.* **1999**, *121*, 10068–10080; c) M. Mitsumi, et al., *Inorg. Chem.* **2009**, *48*, 6680–6691.

[14] a) C.-M. Che, F. H. Herbstein, W. P. Schaefer, R. E. Marsh, H. B. Gray, *J. Am. Chem. Soc.* **1983**, *105*, 4604–4607; b) M. Kurmoo, R. J. H. Clark, *Inorg. Chem.* **1985**, *24*, 4420–4425; c) H. Matsuzaki, T. Matsuoka, H. Kishida, K. Takizawa, H. Miyasaka, K.-i. Sugiura, M. Yamashita, H. Okamoto, *Phys. Rev. Lett.* **2003**, *90*, 046401.

[15] H. Iguchi, S. Takaishi, T. Kajiwara, H. Miyasaka, M. Yamashita, H. Matsuzaki, H. Okamoto, *J. Am. Chem. Soc.* **2008**, *130*, 17668–17669.

[16] N. Kimura, H. Ohki, R. Ikeda, M. Yamashita, *Chem. Phys. Lett.* **1994**, *220*, 40–45.

[17] CCDC 664321 (**2**$\cdot$4H_2O) 745496 (**2**), and 745497 (**3**$\cdot$4H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.